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(54) **A process for the surface treatment of ferrous metal surfaces**

(57) In a process for the surface treatment of ferrous metal surfaces to improve their frictional qualities, wear resistance and resistance to seizing which involves treating the component (10) by electrolysis in which it forms an anode in a bath (12) of molten potassium thiocyanate and sodium thiocyanate, the bath is continuously filtered (20) so as to eliminate insoluble particles of iron sulphides and/or oxides having a diameter greater than 10 μm and to maintain the percentage by weight of the insoluble particles allowed to remain in the bath in the range 0.5% to 2.0% by weight.

FIG.1

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The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.
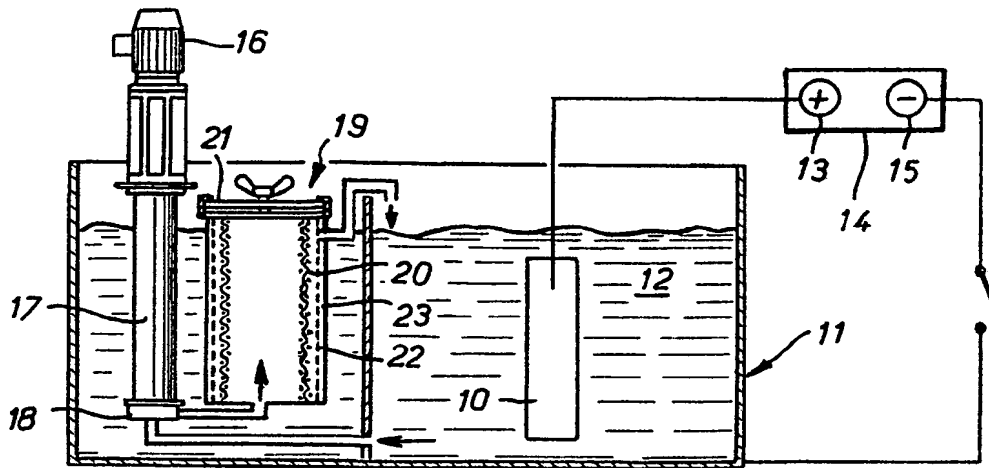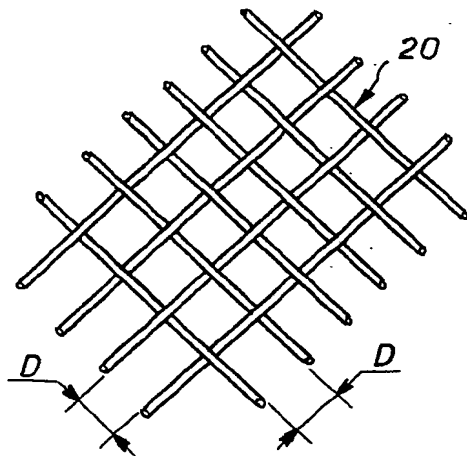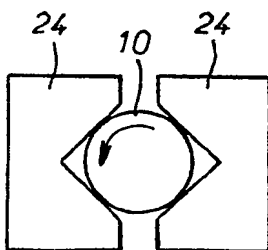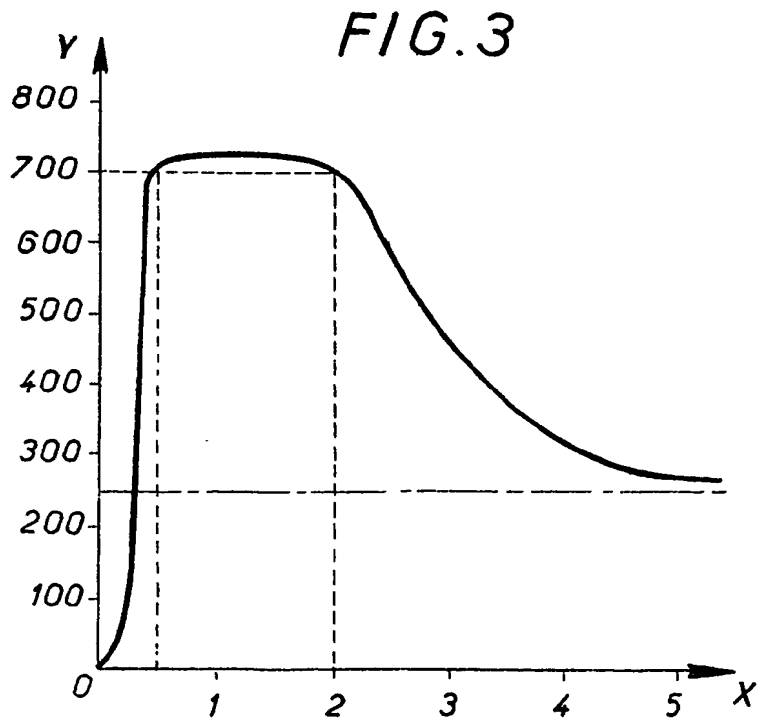
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FIG.1

FIG.2

FIG.3

FIG.4

SPECIFICATION
A process for the surface treatment of ferrous metal surfaces

The present invention relates to a process for surface treatment of ferrous metal surfaces to improve their frictional qualities, wear resistance and resistance to seizing, in which process the said
5 surfaces are treated by electrolysis in which they form an anode in a bath of molten potassium   5
thiocyanate and sodium thiocyanate.
   During the treatment there is formed, on the ferrous metal surface forming the anode, a friction-resistance layer consisting of products of reaction between iron and sulphur, more particularly iron sulphides, especially FeS and FeS_2 which have outstanding seizure-resistance properties.
10   Good results are obtained especially under the following conditions: 10
   (1) The concentrations of potassium thiocyanate and sodium thiocyanate are those of the eutectic mixture, that is to say the bath contains 75 ± 5% KSCN and 25 ± 5% NaSCN, in other words approximately three times as much potassium thiocyanate as sodium thiocyanate;
   (2) The bath working temperature is 195 ± 5°C;
15   (3) The electric current density, which is direct current or rectified alternating current, employed   15
for the electrolysis is between 1.5 and 4.0 A/dm^2;
   (4) The duration of the treatment is between 4 and 20 minutes.
   When operating over an extended period, however, such a bath exhibits the following phenomena:
   — development of the frictional properties of the treated components with time;
20   — development of the physical and chemical properties of the bath itself with time.   20
   With regard to the development of the frictional properties of the treated components with time, it is found that the wear resistance and resistance to seizing of the layers can vary appreciably from one batch of components to another. For example, in Faville-type friction tests in which a cylindrical test-piece 6.5 mm in diameter rotates while clamped between two 90° V-shaped jaws, the measured initial
25   creep loads vary from 700 to 350 daN, depending on the batch of treated components and the time of   25
carrying out the treatment. In all the cases, however, the friction tests are carried out under rigorously identical conditions and all the components have the same visual appearance and the same surface roughness.
   With regard to the development of the physical and chemical properties of the bath itself with
30   time, it is found that, as the treatment of components progresses, the bath fills with insoluble particles, 30
making it necessary, in order to ensure correct treatment of all the components, to increase the time of treatment and to increase the current density. The practical consequences of these increases is an increase in the surface roughness of the treated components and difficulties in treating some components of a complex shape, particularly components having sharp edges, on which the deposits
35   are incorrect owing to point effect.   35
   A progressive lowering of the thermal conductivity of the bath is also observed and it is increasingly difficult, as the bath changes progessively with time, to maintain a uniform temperature throughout the bath.
   A detailed study of all these phenomena has enabled the inventors to demonstrate a direct,
40   remarkable and unexpected correlation between the insolubles content of the bath, the composition of   40
the surface layers formed on the components and the frictional performance of these components.
   Thus, as the insolubles content of the bath progressively increases there is a corresponding increase in the content of iron oxides in the layers, at the expense of their sulphide content.
   Thus, in a bath whose insolubles content is of the order of 1%, the layer consists essentially of the
45   sulphides FeS and FeS_2. With insolubles content of the order of 1.8%, the layer already contains a   45
significant quantity of iron oxides such as FeO and Fe_3O_4. Above 2% of insolubles, the layer contains more and more iron oxides.
   The friction tests carried out in parallel with these analyses show that the performance of the components deteriorates progressively as the content of oxides in the layer increases.
50   Conversely, a bath insolubles content which is too low and below 0.5% results in a quite mediocre   50
performance of the treated components.
   That is, the inventors have demonstrated a remarkable and unexpected optimum effect such that the performance of the treated components in service falls rapidly, below a minimum value and above a well-defined maximum value of the insolubles content of the bath.
55   An object of the present invention is to provide a process for the surface treatment of ferrous   55
metal surfaces which makes it possible to eliminate these various disadvantages and ensures outstanding treatment conditions.
   According to the invention there is provided a process for the surface treatment of ferrous metal surfaces to improve their frictional qualities, wear resistance and resistance to seizing, in which process
60   the said surfaces are treated by electrolysis in which they form an anode in a bath of molten potassium   60
thiocyanate and sodium thiocyanate containing suspended insoluble particles of iron sulphides and/or oxides, characterised in that insoluble particles having a diameter greater than 10 μm are removed from the bath, and the percentage by weight of the insoluble particles which remain in the bath is maintained in the range 0.5% to 2.0% by weight.

By this process layers whose composition is constant from one component to another or from one batch of components to another are obtained on the treated components. These layers are formed essentially from iron sulphides such as FeS and FeS_2, and they are for all intents and purposes free from iron oxides.

5   More particularly the process of the invention ensures that any risk of degradation of the surface   5
quality of the treated components is avoided and the components can be employed without hazard in all industrial applications requiring a good surface quality, for example, tappets, cams and guiding rods especially in the car industry. Furthermore, the components have an outstanding appearance and uniform colour and are clean and free from stains.

10   Preferably the bath is filtered in a closed circuit by means of a filter whose mesh dimensions are   10
between 80 and 150 μm, in order to remove insoluble particles greater than 10 μm and to maintain the percentage by weight of the insoluble particles which remain in the bath below 2.0%. This corresponds to a permeability from 30 to 80 m³/h/m² under a pressure of 50 mm of water.

Preferably, the bath is filtered continuously while the percentage by weight of the insoluble
15   particles is monitored and the filter is changed when this percentage exceeds 2% by weight.   15

The flow rate through the filter may be between 1.5 m³/h and 2.0 m³/h. The surface area of the filter may be between 0.10 m² and 0.30 m², and preferably in the region of 0.20 m².

Further according to the invention, when the percentage by weight of the insoluble particles in the bath is below 0.5%, it is raised to above 0.5% by operating the bath with dummy ferrous metal
20   components for a required time.   20

Some embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings, in which:—

Figure 1 is a diagrammatic view of a treatment bath for carrying out the process of the invention with a means for continuous filtration;
25   Figure 2 illustrates the dimension of the filter mesh;   25

Figure 3 is a diagram showing the performance of the treated components as a function of the percentage of insoluble particles in the bath; and

Figure 4 illustrates diagrammatically a Faville test machine.

Figure 1 shows a treatment bath for the surface treatment of a ferrous metal component 10 to
30   improve their frictional properties, wear resistance and resistance to seizing. The component 10 is   30
immersed in a crucible 11 containing a bath 12 of molten potassium thiocyanate and sodium thiocyanate. The component 10 is treated by electrolysis and forms an anode connected to the positive pole 13 of a source of electric current 14. The crucible 11 is connected to the negative pole 15.

The bath 12 contains approximately three times as much potassium thiocyanate as sodium
35   thiocyanate. The temperature of the bath 12 is of the order of 195°C. The density of the electrolysis   35
current is between 1.5 and 4.0 A/dm². The duration of treatment is between 4 and 20 minutes.

During the electrolysis treatment in which the component 10 to be treated is the anode, the iron in the surface of the component is attached electrochemically by the sulphur originating from the decomposition of the salts in the bath. This sulphiding reaction is accompanied by an additional
40   oxidation reaction due to oxidation by the oxygen present in the bath 12 and originating from the air   40
which dissolves into the free surface of the bath 12.

A proportion of the compounds which are thus formed (sulphides and/or oxides) becomes attached to the surface of the component 10 to be treated and ensures the formation of the layer.

However, another proportion, which is less adherent, is detached and the particles thus formed are
45   dispersed in the bath 12 where they remain in suspension, being insoluble in the molten salts.   45

It is these insolubles consisting of particles of iron sulphides (FeS, FeS_2) and/or iron oxides (FeO, Fe_3O_4), which slowly foul the bath, modifying its properties, and consequently produce a change of the frictional properties of the treated components.

According to the invention, the bath 12 should contain a minimum of insolubles of 0.5% by weight
50   of the bath to a maximum of 2% by weight of the bath.   50

The need for a minimum insolubles content is related to a catalytic effect of the insolubles on the formation of the layer. With a very pure bath no layer is formed on the surface of the components. In fact, the formation of sulphides and/or oxides on the anode surface is produced not by a simple electrochemical process but by a complex reaction chain in which some equilibria are catalysed by the
55   presence of foreign elements, in the present case, the solid particles in suspension.   55

However as soon as the bath 12 becomes over charged with insolubles up to a content greater than 2% by weight, the particles in suspension interfere with the phenomena at the electrodes and particularly at the anode 10 which is the component to be treated. In fact, when iron is oxidised at the anode, it is liable to combine with either the oxygen or the sulphur which are present in the bath. The
60   normal operating conditions of the bath 12 are chosen to favour the sulphuration. The excessive   60
presence of suspended particles in the immediate vicinity of the anode 10 interferes with the electrochemical processes and favours the combination of iron with oxygen at the expense of its combination with sulphur. Consequently, the layers which are formed contain increasing amounts of oxides (FeO, Fe_3O_4) at the expense of the sulphides (FeS, FeS_2) with an accompanying change in the
65   frictional properties of the treated components.   65

The bath 12, containing the insoluble particles of iron sulphides and/or oxides in suspension, is filtered. Such a filtration is carried out in closed circuit to remove the insoluble particles having a diameter greater than 10 μm and to maintain the percentage by weight of the insoluble particles allowed to remain in the bath below 2% whilst, moreover, care is taken that the percentage by weight of the insoluble particles allowed to remain in the bath does not fall below 0.5%. If this percentage falls below 0.5%, provision is made according to the invention to raise it above 0.5% by causing the bath to operate with dummy ferrous metal components for the required time whilst carrying out the filtration process or, preferably, stopping or reducing it.

The bath 12 is filtered continuously whilst the percentage by weight of the insoluble particles is monitored and the filter is changed when this percentage exceeds 2%.

The filtration device is shown diagrammatically in Figure 1. It comprises a motor 16 which drives, through the intermediacy of a driving shaft 17, a vane pump 18 immersed in the bath 12.

The vane pump 18 sucks the salts in the crucible 11 and discharges them inside the filter 19 containing a filtering element 20 locked by a cover 21 and kept in shape by a cylindrical grid 22. A space 23 is provided between the grid and the wall of the filter to collect the clean salts which are then delivered into the working tank.

The constituent components of the filtering device namely the filter body, cover, grid, pipework, are all of stainless steel. The filtering element can be made of various materials, for example a textile fibre or a ceramic fibre or a metal cloth.

Figure 2 shows the filtering element 20 which forms a lattice whose mesh has a dimension D which must be accurate and have a value between 80 and 150 μm. This corresponds to a permeability of 30 to 80 m^3/h/m^2 under a pressure of 50 mm of water.

Below 80 μm, the filtering element blocks very rapidly over a period of a few minutes or a few hours depending on the insolubles content of the bath to be filtered. In practice, such a time space is imcompatible with normal industrial use. If, the mesh of the filtering element exceeds 150 μm, filtration is no longer ensured in practice and none of the insoluble particles contained in the bath are retained.

With a filtering element mesh of between 80 and 150 μm, not only is the insolubles content of the bath kept easily within the range of 0.5 to 2%, but also the filter can function safely for several days, or even several weeks, that is to say in conditions which are compatible with normal industrial use.

The manner in which particles with a diameter of only a few μm can be retained by a filtering element whose mesh is appreciably greater can be explained as follows. During the first moments of filter operation, the particles, which have a more or less pasty consistency, stick to the metallic or textile fibres forming the screen of the filter element. Next, progressively, the new particles which arrive stick in their turn to the preceding particles, and so on till virtually the whole of the filtering element is covered. The layer thus formed is not of an impervious nature and therefore continues to allow the salts to pass and to retain all the new particles coming into contact with it, in the manner of a sponge.

That is, in a remarkable manner, the filtering device simultaneously fulfills two quite distinct functions:—

— it stops and retains the insoluble particles with a diameter greater then 10 μm;

— it allows only a fraction of the particles whose diameter is smaller than 10 μm to pass through, which permits the insolubles content of the bath to be kept in the well-defined range between 0.5 and 2%.

Naturally, these comes a time when the layer of insoluble material retained by the filtering element becomes too great to allow the filtration to take place at an adequate rate. It is then sufficient to withdraw the used filtering element 20 and to replace it with a new one.

In a preferred embodiment, the surface area of the filtering element 20 is between 0.10 m^2 and 0.30 m^2 and preferably in the region of 0.20 m^2, whilst the output of the pump 17 is between 1.5 m^3/h and 2.0 m^3/h, with a delivery pressure of 0.2 to 3 bars. Good results have in particular been obtained with a filtering element 20 having a diameter of 280 mm and a height of 650 mm.

One of the advantages of the device for filtering according to the invention is to limit salt losses. Thus, where a conventional filter (for example paper) gives a salt loss due to retention by the filter of 35 to 40 g/kg of treated components, the loss is only from 5 to 10 g/kg of treated components with the automatic filtering device according to the invention.

EXAMPLES

All the examples described below relate to a bath 12 having the following characteristics:

— composition: 75% KSCN and 25% NaSCN;
— temperature: 195°C;
— current density: 3.2 A/dm^2;
— duration of electrolysis: 10 minutes.

All the friction results, which relate to Faville-type tests, as illustrated in Figure 4, have been obtained by rotating a cylindrical test-piece 10 with a diameter of 6.5 mm, clamped between two jaws 24 with 90° V-notches, in dry air, at a sliding velocity of 0.1 m/s, while increasing uniformly with time the load pressing the jaws against the cylinder.

As the friction increases the test-piece heats up and two phenomena can be produced: either an abrupt seizing, whereupon the test is stopped, or creep of the steel of the cylinder.

It is the load at which this creep beings, called the initial creep load, which is observed and which characterises the frictional performance obtained.

5   EXAMPLE 1   **5**

This example illustrates the role of the insoluble particles present in the bath.

Batches of Faville test-pieces 10 are treated in the baths 12 which differ only in their content of insoluble particles, everything else being kept equal. The results obtained are collated in the following table:

10

Insolubles content of the bath (% by weight)	Initial creep load (daN)
0.1	50 (seizing)
0.3	200
0.5	700
1	710
1.5	715
2	700
2.5	600
3.5	400
5	250

10

15   **15**

20   **20**

These results are illustrated by the curve in Figure 3 in which the insolubles content of the bath 12 in percentages by weight is plotted along the X-axis OX, and the initial creep load, in daN along the Y-axis OY.

This curve clearly illustrates the remarkable and unexpected optimum effect on account of which
25 the service performance of the treated components is outstanding only within a narrow range, between **25**
0.5 and 2%, of the insolubles content of the bath.

It will be noted that in a bath which is very pure, that is to say free from insoluble particles, the test-pieces 10 are not treated; in the friction test they seize instantly.

This example illustrates the whole benefit of operating with a bath 12 whose insolubles content is
30 between 0.5 and 2% by weight. Below 0.5%, the performance of the treated components is quite **30**
mediocre.

Similarly, above 2% it declines very rapidly.

The results of analyses of the layers formed on the components are set out in the following table.

Insolubles content of the bath (% by weight)	Layer thickness (μm)	Layer composition
0.3	2 to 3	FeS:73% FeS$_2$:25% FeO:2%
1	7	·FeS:45% FeS$_2$:50% FeO:5%
1.5	7	FeS:30% FeS$_2$:60% FeO:10%
3.5	6	FeS:25% FeS$_2$:50% FeO:15% Fe$_3$O$_4$:10%

The greater the insolubles content of the bath the more the layers formed on the components are oxidised.

If the proportion of insolubles falls below 0.5% it is increased to above 0.5% by causing the bath 12 to operate as long as required with dummy ferrous metal components as an anode 10, after which the bath is suitable for operating properly with the real components to be treated.

To maintain the proportion of insolubles below 2%, use is made of the filtering device described with reference to Figure 1.

EXAMPLE 2

This example illustrates the advantage produced when the diameter of the insoluble particles present in the bath does not exceed 10 μm.

The tests are carried out in two baths with the same composition under the same conditions of electrolysis and with the same insolubles content of 1.5% by weight. In one case the bath is filtered with a filtering element having a mesh dimension of 90 μm, while in the other case a filter with a mesh dimension of 200 μm is used which allows the particles of large dimensions to pass. To obtain the same insolubles content in both cases it suffices to allow the first bath to operate longer than the second.

Micrographic examination of samples taken from the baths confirms that no particles of diameter greater than 10 μm are present in the first case. Similarly, it is confirmed that much larger particles, up to 30 to 40 μm are present in the second bath.

Components which are identical in all respects and have an initial surface roughness of 0.3 μm are treated in these two baths.

After treatment the following observations are made:

(a) *First bath* (insoluble particles smaller than 10 μm),
— components coloured black, uniform;
— do not stain when handled;
— surface roughness: 0.6 μm.

(b) *Second bath* (insoluble particles larger than 10 μm),
— components irregularly coloured, with haloes;
— staining when handled;
— surface roughness: 2.8 μm.

EXAMPLE 3

This example illustrates the role of the mesh dimension D, Figure 2, of the filtering element 20.
A bath which is deliberately heavily loaded with insolubles is used at the outset; initial content 4%

by weight.
    Various filtration tests are carried out with the use of filtering elements with a metal lattice whose
mesh dimensions are respectively 30, 70, 80, 100, 150, 200 and 250 μm.
    The following results are obtained:
5   — 30 μm mesh: filter blockage after 1/2 hours operation;   5
    — 70 μm mesh: filter blockage after 2 hours;
    — 80, 100 and 150 μm meshes: the insolubles content of the bath is reduced to 2% after 10
hours operation. It then continues to drop progressively to stabilise at 1.3% after 15 hours. The filter
then continues to operate normally for 9 days, with an insolubles content in the bath remaining constant
10 at 1.3%. At the end of these 9 days a slow and progressive rise in the insolubles content takes place   10
over a further 4 days. The filter is changed at the end of 15 days;
    — 200 μm mesh: the filter still functions, but allows particles with a diameter greater than 10 μm
to pass;
    — 250 μm mesh: the filter is practically inoperative and does not retain the insolubles.
15.   It has been possible to examine the effect of other parameters of the treatment under reproducible   15
experimental conditions because of the control of the insolubles content which has eliminated a major
cause of random variations of the results.
    It has been possible to confirm that the friction performance of the components is practically
stabilised after a minimum duration of treatment of three to four minutes. In particular this makes
20 possible bulk processing or barrel processing, in which the effective duration of anodic treatment varies 20
widely for different components of the same batch.
    The effect of the current density has been studied by varying this current density between 0.5 and
8 amperes per square decimetre (A/dm^2, a conventional unit in electrolytic processing). It was found
qualitatively that the protective layer consisting of sulphides and oxides had an oxide content which
25 increased with the current density; the surface roughness of the components increased in parallel. More   25
precisely, the surface roughness, after a fairly rapid increase with the current density up to
approximately 1.5 A/dm^2, formed a virtual plateau up to approximately 5 A/dm^2; above this current
density the roughness increased more rapidly. The surface roughness plateau corresponds to a layer
composition which is relatively constant and in equilibrium with regard to oxides and sulphides. In
30 parallel with this, the friction performance, determined using the means indicated above, has a fairly flat 30
optimum for current densities between 1.5 and 4.0 A/dm^2.

CLAIMS
    1. A process for the surface treatment of ferrous metal surfaces to improve their frictional
qualities, wear resistance and resistance to seizing, in which the said surfaces are treated by electrolysis
35 in which they form an anode in a bath of molten potassium thiocyanate and sodium thiocyanate   35
containing suspended insoluble particles of iron sulphides and/or oxides, characterised in that insoluble
particles having a diameter greater than 10 μm are removed from the bath, and the percentage by
weight of the insoluble particles which remain in the bath is maintained in the range 0.5% to 2.0% by
weight.
40   2. A process according to Claim 1, characterised in that the bath is filtered in a closed circuit by   40
means of a filter whose mesh dimensions are between 80 and 150 μm, to remove insoluble particles
having a diameter greater than 10 μm from the bath and to maintain the percentage by weight of the
insoluble particles which remain in the bath below 2%.
    3. A process according to Claim 2, characterised in that the bath is filtered continuously while the
45 percentage by weight of the insoluble particles is monitored and in that the filter is changed when this   45
percentage exceeds 2% by weight.
    4. A process according to Claim 2 or Claim 3, characterised in that the flow rate through the filter
is between 1.5 m^3/h and 2.0 m^3/h.
    5. A process according to Claim 4, characterised in that the surface area of the filter is between
50 0.10 m^2 and 0.30 m^2, and preferably in the region of 0.20 m^2.   50
    6. A process according to any one of Claims 1 to 5, characterized in that when the percentage by
weight of the insoluble particles in the bath is below 0.5%, it is raised to above 0.5% by operating the
bath with dummy ferrous metal components for a required time.
    7. A process according to any one of the preceding claims, characterised in that, the bath contains
55 potassium thiocyanate in a quantity which is approximately three times that of sodium thiocyanate, the   55
bath temperature is of the order of 195°C, the electrolysis current density is between 1.5 and
4.0 A/dm^2 and the duration of treatment is between 4 and 20 minutes.
    8. A process for the surface treatment of ferrous metal surfaces, substantially as herein described
with reference to the accompanying drawings.